

IMPLICATIONS OF FUEL CROSSOVER IN DIRECT METHANOL FUEL CELLS

S. R. Narayanan, E. Vamos, S. Surampudi, H. Frank and G. Halpert

*Jet Propulsion Laboratory,
California Institute of Technology,
4800 Oak Grove Drive, Pasadena, CA 91109*

A new liquid-feed type direct methanol fuel cell using proton-exchange membrane electrolyte was developed at JPL, under an AWA-sponsored program [1,2]. This fuel cell operates on aqueous solutions of methanol and delivers 0.540 V at 0.1 A cm⁻² and 0.500V at 0.28 A cm⁻² at 95 °C. In this design an aqueous solution of methanol (0.5-2.0M) is circulated past the platinum alloy anode of a polymer electrolyte membrane assembly. Oxygen is supplied to the platinum cathode at pressures of 20-50 psig. The important desirable features of this liquid-feed design are: 1. Being free of liquid acid electrolyte (unlike the many earlier liquid-feed versions) the cell can be scaled into a stack with no parasitic shunt currents. 2. The water content of the proton-exchange membrane is maintained by the aqueous methanol solution. 3. Separation of the gaseous carbon dioxide from the liquid reactants (unlike in gas-feed cells).

Since methanol can dissolve readily in water and permeates through the proton-exchange membrane, some fraction of the fuel solution crosses over to the cathode side. This is not a problem special to the liquid feed design and would be encountered with the gas-feed design and fuels other than methanol so long as they are soluble to a finite extent in water. In the present study we measure the rate of crossover and understand the consequences of this phenomenon.

Since the potential of the cathode is 0.9 V positive to the standard reduction potential of the CH₃OH/CO₂ reaction, the oxidation of methanol occurs to carbon dioxide. Gas chromatographic analysis of the vented oxygen on the cathode side shows large amounts of carbon dioxide and trace amounts of methanol; the amount of methanol being less than 0.1% of the amount of carbon dioxide. This observation is independent of whether the fuel cell is on open circuit or on load. These findings show that all the methanol reaching the cathode by crossover is completely converted to carbon dioxide and the conversion results in a zero methanol concentration at the cathode/electrolyte interface. Under steady-state conditions, the rate of methanol crossover becomes then linearly dependent on the concentration of the fuel and is determined by the diffusion coefficient and solubility of the fuel in the proton exchange membrane.

Effect of crossover on the performance of direct methanol fuel cells:

The performance of the liquid feed direct methanol fuel cell at various methanol concentrations is shown in Fig. 1. The kinetics of methanol oxidation at the Pt/Ru anode is found to improve significantly with increased concentration (Fig. 2) and current densities as high as 0.4 A cm⁻² can be sustained at 4 M methanol concentration. However, it is found that as the concentration of methanol increases the amount of methanol crossing over to the oxygen electrode increases. The mixed potential of the oxygen electrode (determined by methanol oxidation and oxygen reduction reactions) is then found to decrease as the electrochemical rates of methanol oxidation at the cathode increase. Therefore, lowering of the crossover rates will permit the operation of the cells at a higher voltage and current density.

Measurement of crossover rates:

The steady-state crossover rate for various concentrations of methanol was measured by estimating the carbon dioxide evolution rate on the cathode side. The carbon dioxide evolved at the cathode and transported in the oxygen stream was absorbed in a solution of barium hydroxide. The excess barium hydroxide is then back titrated with strong acid. The reproducibility of crossover rates measured by this method is in the range of 3-4%. Figure 3 shows the dependence of crossover rate on concentration and the gradient of this curve is parameter characteristic of the membrane electrode assembly. The increase of temperature results in an increased crossover rate as shown in Fig. 3.

In a fuel cell operating in the multipass mode where the solution is re-circulated several times past the anode until it is depleted of methanol, the crossover rate continuously decreases with time. Under constant current conditions the variation of crossover rate with time is given by,

$$R = (nFkC^* + i) \exp(-kpt) - i$$

where R is the crossover rate expressed in A cm⁻², i is the constant current density, k is a parameter characteristic of the crossover properties of the membrane electrode assembly and the fuel and has the units of s⁻¹ cm, C^* is concentration at $t=0$, and P = area of electrodes/volume of solution. The variation of concentration with time in such an experiment can be used to measure the crossover parameter using the following relation $k = (1/C^*) \{ (i/nF) - (1/P)(dC/dt)_{t \rightarrow 0} \}$

The value of k determined from carbon dioxide measurements are in good agreement with that determined by the concentration-time method.

Effect of crossover on utilization:

The utilization of fuel under constant current and constant concentration conditions with crossover would be given by,

$$U = i / (i + nFkC^*) \quad [1]$$

The utilization decreases as the concentration is increased and increases with current density. However, in a constant current mode of operation where the concentration of methanol is allowed to deplete until no more of the solution can be utilized, the utilization would be given by,

$$U = (i/nFkC^*) \ln \{ (nFkC^* + i) / (nFkC_{lim} + i) \} \quad [2]$$

where C_{lim} is the limiting concentration permissible for sustaining the current density i . The utilization calculated from Eq. [2] as a function of initial concentration C^* at various values of i and C_{lim} and crossover parameter $k = 0.0001165 \text{ s}^{-1} \text{ cm}$ (derived from experiment), are shown in Fig. 4. The utilization is expected to increase with increasing initial concentration especially for current densities greater than 0.05 A cm⁻², and reaches a maximum which is different for each concentration. Experimental results on utilization studies will be presented.

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References

1. S. R. Narayanan, E. Vamos, S. Surampudi, H. Frank and G. Halpert, Presentation at the Fuel Cell Seminar, Tucson, AZ, Dec 1, 1992.
2. E. Vamos, S. R. Narayanan, S. Surampudi, H. Frank and G. Halpert, Presentation at the Conference on Advances in Batteries and Applications, Long Beach, CA, Jan 14, 1993.

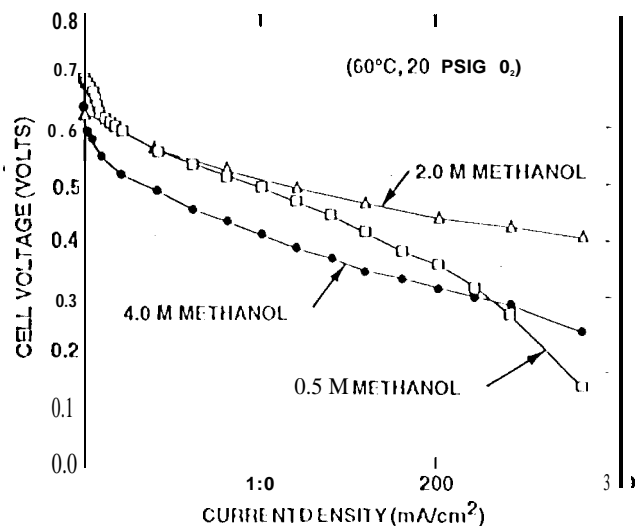


Fig. 1: Effect of methanol concentration on fuel cell performance; anode Pt-Ru/ cathode Pt

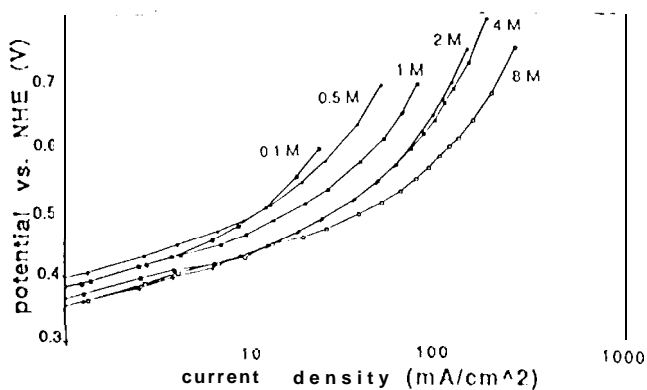


Fig. 2: Steady-state galvanostatic polarization curves for electro-oxidation of methanol in 0.5M sulfuric acid at Pt-Ru ($5\text{mg}/\text{cm}^2$) at various methanol concentrations and 250 C

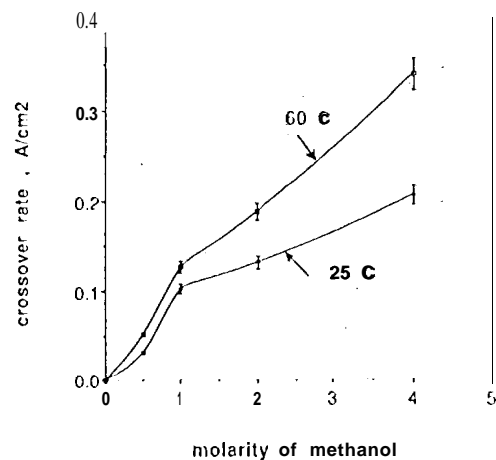


Fig. 3: Dependence of crossover rate on methanol concentration and temperature in liquid-feed fuel cell

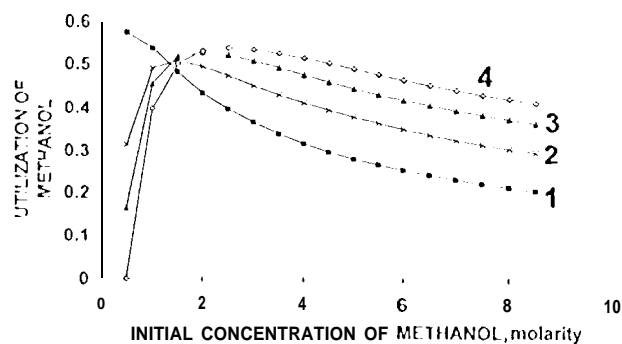


Fig. 4: Predicted dependence of utilization (Eq. [2]) on initial concentration of methanol in null pass concentration-depleting type operation. The value of crossover parameter was experimentally determined ($0.0001165\text{ s}^{-1}\text{ cm}$). The value of i and C_{lim} for the curves are as follows: 1: $0.05\text{ A}/\text{cm}^2$ and 0.1 M ; 2: $0.1\text{ A}/\text{cm}^2$ and 0.3 M ; 3: $0.15\text{ A}/\text{cm}^2$ and 0.4 M ; 4: $0.2\text{ A}/\text{cm}^2$ and 0.5 M